

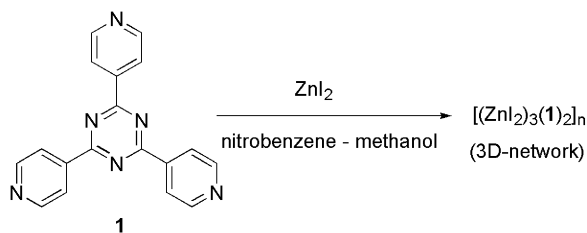
Crystal-to-Crystal Guest Exchange of Large Organic Molecules within a 3D Coordination Network

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Porous coordination networks are a new class of organic–inorganic hybrids that are designable and capable of various functions^{1,2} such as separation,^{2a} ion exchange,^{2b} catalysis,^{2c,d} and gas adsorption.^{2e} One recent topic in this area is their dynamic properties responsive to guest inclusion, exchange, or removal,^{3–5} which have been often studied by spectroscopy, powder X-ray diffraction, or both. Recently, we and others have analyzed the guest exchange/inclusion processes in a single-crystal-to-single-crystal fashion.^{3a–h,4,5} Until now, however, guests have been limited only to small molecules. Effective inclusion of large molecules,^{6,7} as well as the observation of the inclusion process by X-ray crystallography, is essential to the design of sophisticated functional materials, in which the structural information at the atomic level plays a crucial role. Here we report the single-crystal-to-single-crystal guest exchange of large organic molecules within a porous 3D coordination network, $[(ZnI_2)_3(\mathbf{1})_2]$, where **1** is 2,4,6-tris(4-pyridyl)triazine. The synthesis and structure of the nitrobenzene clathrate, $\{[(ZnI_2)_3(\mathbf{1})_2] \cdot 5.5(\text{nitrobenzene})\}$ (**2**), and the dynamic behavior of **2** via guest removal and re-inclusion have been previously studied.^{3a,8}



The 3D net of **2** possesses large pores filled by nitrobenzene columns (Figure 1a). When single crystals of **2** were immersed in a saturated cyclohexane solution of triphenylene (**3a**) at room temperature for 24 h, the crystal color of **2** turned pale yellow. The crystals showed no change in size and morphology and, after isolation, diffracted well for single-crystal X-ray study. The crystallographic analysis revealed the structure of the inclusion complex $\{[(ZnI_2)_3(\mathbf{1})_2] \cdot 1.5(\mathbf{3a}) \cdot 2.5(\text{cyclohexane})\}$ (**4a**), indicating single-crystal-to-single-crystal guest exchange from nitrobenzene to a mixture of **3a** and cyclohexane (Figure 1b).⁹ Despite the inclusion of the large guest, the 3D net remains unchanged, and the cell parameters are almost the same as those of **2**. The guest molecule (**3a**) is found in three independent positions A, B, and C as shown in Figure 1b.¹⁰ Position A is approximately perpendicular to the *a* + *c* direction. Positions B and C are approximately parallel to each other and to ligand **1**. In both positions B and C, the distance between **3a** and **1** is 3.4 Å, which is slightly shorter than the sum of van der Waals radii (3.5 Å) (Figure 1c).

In a similar way, anthracene (**3b**) and perylene (**3c**) also replaced nitrobenzene in **2** to give the inclusion complexes $\{[(ZnI_2)_3(\mathbf{1})_2] \cdot 1.4(\mathbf{3b}) \cdot 2.2(\text{cyclohexane})\}$ (**4b**) and $\{[(ZnI_2)_3(\mathbf{1})_2] \cdot (\mathbf{3c}) \cdot (\text{cyclohexane}) \cdot$

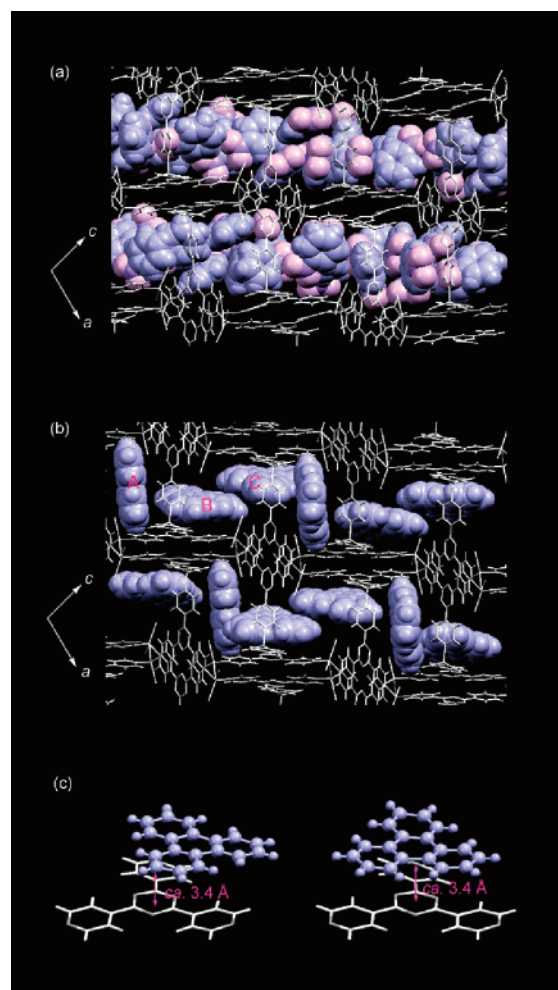


Figure 1. (a) Before guest exchange: crystal structure of **2** accommodating nitrobenzene molecules. (b) After guest exchange: crystal structure of **4a** accommodating triphenylene molecules. Cyclohexanes are omitted for clarity. (c) Views showing π – π interaction between ligand **1** (in **4a**) and guest **3a** at the position of B (left) and C (right).

$\cdot 1.5(\text{nitrobenzene})\}$ (**4c**), respectively, without loss of crystallinity. Crystallographic analysis showed efficient stacking of the guest and ligand (Figure 2a,b). Close ligand–guest contact suggests donor–acceptor interaction between the electron-rich guests (**3b,c**) and the electron-deficient ligand (**1**).

The donor–acceptor interactions were strongly supported by a significant color change during the formation of the inclusion complex. Anthracene included crystals (**4b**) are deep yellow, whereas **2** and **3b** are both colorless. The diffuse reflectance UV–vis spectrum of **4b** showed a new absorption band in the 400–600 nm region. The absorption edge is red-shifted by 170 nm as

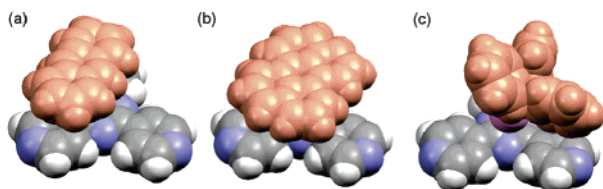


Figure 2. Partial structures of **4b**, **4c**, and **4d**. The occupancy of each guest molecule: (a) 0.39(2) for **4b**, (b) 1.0 for **4c**, and (c) 0.50(1) for **4d**.

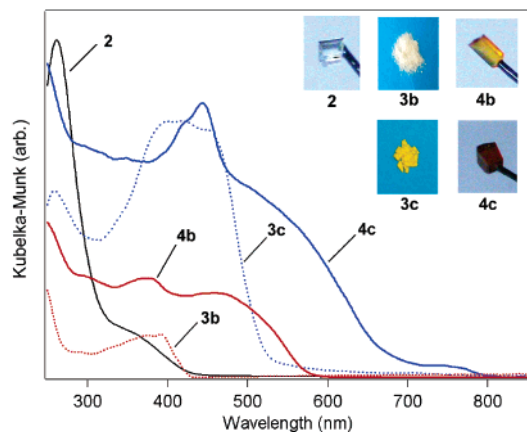


Figure 3. Change of the crystal color. Diffuse reflectance UV-vis spectra of **2**, **3b**, **4b**, **3c**, and **4c**.

compared with that of anthracene (**3b**) (Figure 3). In the case of perylene complex (**4c**), the color changed to deep red and the absorption band was significantly red-shifted, reaching 800 nm.

DFT calculations showed that the phases of the HOMO of guests (**3a–c**) effectively matched those of the LUMO of the simplified model framework of **2**,¹¹ allowing donor–acceptor interactions. Also, the half-oxidation potentials of the guest molecules (**3a–c**) are in the following order: **3a** (1.55 V), **3b** (1.09 V), and **3c** (0.85 V).¹² As expected, as the HOMO–LUMO gap is smaller, the shift of the absorption band is larger (Figures 3, S6, and S7). Therefore, it is clear that crystal color change is attributed to the formation of charge-transfer complexes.

Another large guest included in **2** was triphenylphosphine oxide (**3d**). In this case, no color change was observed during the formation of the inclusion complex $\{[(\text{ZnI}_2)_3(\mathbf{1})_2] \cdot 1.3(\mathbf{3d})\}$ (**4d**).¹³ The crystallographic analysis clearly indicated the absence of aromatic stacking between the nonplanar guest of **3d** and the ligand of **1** (Figure 2c). Alternatively, the electron-donating oxygen atom of **3d** is situated above the ligand at 3.0 Å.

The inclusion of large guest also took place in a dynamic fashion from a contracted form of $[(\text{ZnI}_2)_3(\mathbf{1})_2]$ net. We have previously reported that this network contracts and expands by the removal and re-inclusion of nitrobenzene guests.^{3a} When a single crystal of the contracted structure $\{[(\text{ZnI}_2)_3(\mathbf{1})_2] \cdot 3.3(\text{nitrobenzene})\}$ (**2'**) was treated with a saturated cyclohexane solution of **3a** at room temperature for 24 h, the network expanded and the inclusion complex (**4a**) was formed, as confirmed by X-ray analysis. Noteworthy is that inclusion complexes (**4a–d**) were obtained only via guest exchange. For example, one pot complexation of ZnI_2 and **1** in the presence of **3a** resulted in the formation of another complex, which was completely different from **4a**.¹⁴

In summary, we demonstrate the efficient inclusion of large guest molecules in the large channel of **2** via single-crystal-to-single-crystal guest exchange. Our findings demonstrate that interaction strongly controls the inclusion geometry of the guest molecules. Such intermolecular interactions as characterized by X-ray analysis will be helpful for design of not only simple inclusion phenomena but also new physical properties and chemical reactions within the coordination network.

Acknowledgment. This work was supported by Japan Science and Technology Agency (JST).

Supporting Information Available: Experimental details, UV-vis spectral change in guest exchange processes, figures of the HOMO–LUMOs of **4a–c**, and molecular structures of **4a–d**. The crystallographic details are described in the CIF files deposited in CCSD (No. 241417-241420). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Triphenylenes are found in the positions of **B** and **C** with 50% occupancy.
- (11) The simplified model of **2**, $[(\text{ZnI}_2)_3(\mathbf{1})(\text{pyridine})_3]$, was optimized at the B3LYP level of theory with the SDD basis set for Zn and I. See Supporting Information.
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- (14) This structure will be reported elsewhere.

JA046478A